

**REMARKS**

By the present communication, Claims 1, 8 and 17 have been amended and Claims 32-34 added to define Applicant's invention with greater particularity. Claims 25-31 have been canceled without prejudice. Applicant expressly reserves the right to pursue the subject matter of the canceled claims in a timely filed divisional. Claims 1-24 and 32-34 are pending.

Support for the amendments and new claims is found throughout the application as filed including, but not limited to:

Claim 1	Paragraphs 25, 26, 27 and Examples 1, 2 and 4.
Claim 8, 17	Paragraphs 6, 8, 24-29 and the Examples.
Claims 32-35	Claims 8, 13-15, 18 and 20 as originally written.

Applicant respectfully requests reconsideration of the present application in view of the foregoing amendments and in view of the reasons that follow.

***I. Objections to Claims***

The objection to Claim 11 because "talc is not a phyllosilicate" (Office Action, page 3) is respectfully traversed. As shown by the enclosed copy of Table 1.1 from "Formation and Properties of Clay-Polymer Complexes" (B.K.G. Theng, Elsevier, NY, 1979), talc is indeed considered a phyllosilicate by those of skill in the art. Applicant respectfully requests this objection be withdrawn.

The objection to Claim 17 because "term 'in compatible solvent' is repeated twice" (Office Action, page 3) is respectfully traversed. Although Applicant asserts that the phrase at issue was properly repeated, to advance prosecution the claim has been amended to state in part

"dissolving a polymer in the compatible solvent." The scope of this element is broadened or remains unchanged by the amendment and the element is entitled to a full range of equivalents.

Applicant respectfully requests this objection be withdrawn.

## ***II. Claim Rejections Under 35 U.S.C. § 112, second paragraph***

The rejections of Claims 4, 13 and 20 under 35 U.S.C. § 112, second paragraph as allegedly being indefinite for failing to particularly point out and distinctly claim the subject matter which Applicant regards as the invention is respectfully traversed. With regards to Claim 4 and the term "monoalkyl ether derivatives" of polyethylene glycol and polypropylene glycol the Office Action states "first, term monoalkyl ether alone is not a polymer. Second, use of the term "derivative" renders claim indefinite since it is not clear as to what type of polymer applicants are referring to." Office Action, page 2. Applicant respectfully disagrees with the Examiner's assertion. As the Examiner is aware, polyethylene glycol (PEG) and polypropylene glycol are linear alkyleneoxy polymers terminated at each end by a hydroxyl group. As is well known to those of ordinary skill in the art, derivatives of polyethylene and polypropylene glycol may be prepared in which only a single terminal hydroxyl group has been alkylated. In fact, such monoalkyl ether derivatives are commercially available and Applicant has enclosed a product sheet from the Dow Chemical Company showing exactly such products. For example, Table A in the product sheet shows that the monoethyl, monobutyl and monoethyl ethers of polyethylene glycol are available as well as lower molecular weight methyl and ethyl ether PEG derivatives. Similarly, Table B shows that lower molecular weight polypropylene glycol, monoethyl and monopropyl derivatives are available. Thus, Applicant respectfully submits that those skilled in the art readily understand what type of polymer is being referred to in Claim 4 by the language "polyethylene glycol, polypropylene glycol and monoalkyl ether derivatives thereof."

Applicant respectfully disagrees with the Examiner's contention that Claim 13 is indefinite with respect to polyethylene glycol based surfactants and polypropylene glycol based surfactants. Applicant's disclosure at paragraph 31 on page 12 of the application teaches that

such surfactants include polyethylene-block-polyethylene glycol or polypropylene-block-polyethylene glycol. Accordingly, those of ordinary skill in the art will understand that polyethylene glycol based surfactants and polypropylene glycol based surfactants refer to block co-polymers of polyolefins with either polyethylene glycol or polypropylene glycol.

Applicant respectfully disagrees that the phrase "less than about 2% of water" renders Claim 20 indefinite. The Office Action stated that it is "not clear if applicants require the amount of water to be less than 2% or about 2%." Office Action, page 3. However, as the MPEP points out "the fact that claimed language including terms of degree may not be precise does not automatically render the claims indefinite." MPEP 2173.05(b), Relative Terminology. "Mathematical precision should not be imposed for its own sake; a patentee has the right to claim the invention in terms that would be understood by persons of skilled in the field of the invention." *Modine Mfg. Co. v. U.S. Intern. Trade Com'n*, 75 F.3d 1545, 2557 (Fed. Cir. 1996). Applicant respectfully submits that one of ordinary skill in the art would understand the meaning of the phrase at issue based on its plain meaning and the Applicant's disclosure. At paragraph 45, page 19 Applicant teaches "as will be understood by one skilled in the art all language such as "up to," "at least," "greater than," "less than," and the like include the numbers cited and refer to ranges which can be subsequently broken down into sub-ranges . . ." (Emphasis added.) Thus, in Claim 20 the phrase "less than about 2% water" will include not only those compositions having less than 2% water but those having about 2% water as well. Accordingly, Claim 20 is clear as written and Applicant respectfully requests the withdrawal of this ground of rejection.

### ***III. Claim Rejections Under 35 U.S.C. § 102***

The rejection of Claims 1-7 under 35 U.S.C. § 102(b) as allegedly being anticipated by Beall (U.S. Patent No. 5,552,469) is respectfully traversed. Applicant's invention as defined by Claim 1 distinguishes over Beall by reciting a phyllosilicate-polymer composition comprising: (a) a phyllosilicate; and (b) a polymer layer absorbed onto the basal surface of the phyllosilicate providing a phyllosilicate-polymer composition, wherein the polymer of the polymer layer exists

as an oxonium cation on the basal surface, the phyllosilicate-polymer composition is present as a single phyllosilicate-polymer phase and the phyllosilicate-polymer composition exhibits an anomalous basal spacing. Beall simply does not teach nanocomposites comprising the polymer layer of the present invention.

Specifically, Beall fails to disclose polymers adsorbed onto the basal surface of a phyllosilicate as oxonium ions. Nor does this reference teach any polymers that inherently have this property. For example, although Beall's list of suitable polymers goes on for 228 lines (Col. 9, Ln. 41- Col. 12, Ln. 67), nowhere does he teach or suggest the use of polyethylene glycol, polypropylene glycol or monoalkyl ether derivatives thereof for use in nanocomposites. Therefore, Beall does not disclose each and every element of the claimed invention and Applicant respectfully requests that this ground of rejection be withdrawn.

The rejections of Claims 1-8, 10-12, 16-18, 21, 22 and 24 under 35 U.S.C. § 102(e) as allegedly anticipated by Blanton (U.S. Patent No. 6,555,610) is respectfully traversed. Applicant's invention as defined by Claim 1 distinguishes over Blanton by reciting a phyllosilicate-polymer composition comprising: (a) a phyllosilicate; and (b) a polymer layer adsorbed onto the basal surface of the phyllosilicate providing a phyllosilicate-polymer composition, wherein the polymer layer is formed by adsorption of the polymer as an oxonium cation onto the basal surface, the phyllosilicate-polymer composition is present as a single phyllosilicate-polymer phase and the phyllosilicate-polymer composition exhibits an anomalous basal spacing. Claim 4 further distinguishes over Blanton by reciting that the polymer is selected from the group consisting of polyethylene glycol, polypropylene glycol and monoalkyl ether derivatives thereof. Claim 7 still further distinguishes over Blanton by reciting that the basal spacing of the phyllosilicate-polymer composition increases as the molecular weight of the polymer increases. Blanton fails to disclose or suggest any of these phyllosilicate-polymer compositions.

In contrast to the phyllosilicate-polymer compositions contemplated by the present claims, Blanton discloses a method to produce reduced crystallinity polyethylene oxide with intercalated clay. Blanton teaches:

mixing smectite clay and polyvinyl pyrrolidone to form a first dispersion of intercalated clay, mixing said dispersion with polyethylene oxide to form a second dispersion, flowing said second dispersion into ketone so as to flocculate a polymer composite of polyethylene oxide and intercalated clay and recovering said flocculate.

(Blanton, Claim 1.) As those skilled in the art would recognize based on Applicant's disclosure, under the conditions disclosed by Blanton, neither polyvinyl pyrrolidone nor polyethylene oxide adsorb onto the basal surface of the clay as an oxonium cation. Specifically, the synthetic smectite clays utilized by Blanton exist wholly in the  $\text{Na}^+$  form and prevent adsorption onto their basal surface by the polymers as oxonium cations. (As shown in Example 1 of the present application, complete sodium exchange of a nanocomposite of the invention destroyed the anomalous basal spacing by preventing adsorption of the polymer as an oxonium cation.) Therefore, the nanocomposite disclosed by Blanton lacks the polymer layer formed by adsorption of the polymer as an oxonium cation onto the basal surface of the phyllosilicate as recited by Claims 1-7 of the present invention. Furthermore, Blanton discloses the use of polyvinyl pyrrolidone and polyethylene oxide but not the use of polyethylene glycol, polypropylene glycol and monoalkyl ether derivatives thereof as contemplated by the present invention as defined by Claim 4.

Finally, the statement in the Office Action that "it would be inherent that the bigger the polymer the more of it one has to intercalate in between the platelet hence, the increase in basal spacing" is simply wrong. For example, as taught in Example 2 of the present application, previous clay-polymer intercalates of polyethylene oxide and polyethylene glycol display a constant basal spacing of about 17.7 Å that is independent of the molecular weight of the polymer. See, e.g. Vaia et al. *Adv. Mater.* (1995), 7, 154 (a copy of which is enclosed). Only where, as in the present invention, a specific stoichiometry exists between the polymer and clay

will the basal spacing increase with increasing molecular weight of the intercalating polymer. Accordingly, Blanton fails to teach each and every element of Claims 1-7.

Moreover, Claims 8, 10-12 and 16 distinguish over Blanton by reciting at least an anisotropic liquid crystalline composite, comprising: (a) a phyllosilicate-polymer composite, comprising; (1) a phyllosilicate; and (2) a polymer adsorbed onto the phyllosilicate, wherein the polymer is selected from polyethylene glycol, polypropylene glycol or monoalkyl ether derivatives thereof, and the phyllosilicate-polymer composite is birefringent. Blanton does not disclose or suggest a liquid crystalline composite as defined by Claims 8, 10-12 and 16.

In contrast to the liquid crystalline composites contemplated by the present claims, Blanton does not teach or suggest the present liquid crystal composites comprising a polymer selected from polyethylene glycol, polypropylene glycol or monoalkyl ether derivatives thereof. Instead, Blanton discloses only nanocomposites prepared from polypyrrolidone and polyethylene oxide (PEO) wherein the PEO has reduced crystallinity. In fact, the method of Blanton produces a flocculate which by definition has no long range order; and the nanocomposite is therefore amorphous in structure. As those of skill in the art would recognize, such amorphous composites are incapable of increasing gas barrier properties of the polymer. Hence, Blanton fails to teach each and every element of Claims 8, 10-12 and 16.

Similarly, Blanton fails to anticipate Claims 17, 18, 21, 22 and 24. Claim 17 and its dependent claims distinguish over Blanton by reciting a method for producing an anisotropic liquid crystalline composite from a phyllosilicate and a polymer comprising: (a) suspending a phyllosilicate in a compatible solvent; (b) dissolving a polymer in the compatible solvent, wherein the polymer is selected from polyethylene glycol, polypropylene glycol or monoalkyl ether derivatives thereof; and (c) removing a sufficient amount of the compatible solvent to produce an anisotropic liquid crystalline composite. In contrast, the method disclosed by Blanton simply does not teach the use of polyethylene glycol, polypropylene glycol and monoalkyl ether derivatives thereof to form liquid crystalline nanocomposites. Thus, Blanton again fails to teach each and every element of Claims 17, 18, 21, 22 and 24. Accordingly, Applicant respectfully

requests reconsideration and withdrawal of the rejection of Claims 1-8, 10-12, 16-18, 21, 22 and 24 under 35 U.S.C. § 102(e).

The rejection of Claims 1-3, 7-9, 15 and 16 under 35 U.S.C. § 102(b) as allegedly being anticipated by Carter (U.S. Patent No. 5,229,451) is respectfully traversed. As with Beall above, the present invention as defined by Claims 1-3 distinguishes over Carter by reciting in part a nanocomposite in which "the polymer layer is formed by adsorption of the polymer as an oxonium cation onto the basal surface" of the phyllosilicate. In contrast, Carter discloses liquid crystal polymers such as "wholly aromatic polyesters, aromatic-aliphatic polyesters, aromatic polyazomethines, aromatic polyester-carbonates and wholly or non-wholly aromatic polyester-amides." Carter, Col. 7, Ln. 61-65. Nowhere does Carter disclose a nanocomposite having a polymer layer formed by the adsorption of the polymer as an oxonium cation onto the basal surface. In addition, Carter fails to disclose the polymers recited in Claims 8, 9, 15 and 16 wherein the polymer is selected from the group consisting of polyethylene glycol, polypropylene glycol and monoalkyl ether derivatives thereof. Thus, Carter fails to teach each and every element of the present claims. Accordingly, reconsideration and withdrawal of this ground of rejection is respectfully requested.

#### *IV. Objections to Claims*

Applicant welcomes the Examiner's determination that Claims 13, 14, 19, and 20 are allowable if rewritten in independent form. Applicant has rewritten Claims 13, 14, 15, and 20 as new Claims 32, 33, 34, and 35 respectively, to include all the elements of the base claims (Claims 8 and claim 17) and any intervening claims. Although Claim 15 was rejected rather than objected to, Applicant notes that Claim 15 depended from objected to Claim 13. Because the Examiner found Claim 13 patentable over the prior art, Claim 15, which includes all the elements of Claim 13, must also be patentable over the prior art. Accordingly, Applicant respectfully submits that Claims 32-35 are patentable and requests the allowance thereof.

Furthermore, in view of the amendment to Claim 17 and remarks above (Section III), it is respectfully submitted that Claim 19, which depends from Claim 17, is in condition for allowance. Applicant therefore requests that the Examiner withdraw the objection to Claim 19.

**V. Conclusion**

In view of the above amendments and remarks, reconsideration and favorable action on all claims are respectfully requested. If any issue remain to be resolved in view of this response, the Examiner is invited to contact the undersigned at the telephone number set forth below so a prompt disposition of this application can be achieved.

Respectfully submitted,

Date September 23, 2003

By Mark A. Kassel

FOLEY & LARDNER  
Customer Number: 23524  
Telephone: (608) 258-4272  
Facsimile: (608) 258-4258

Mark A. Kassel  
Attorney for Applicant  
Registration No. 38,200



*Developments in Soil Science 9*

# FORMATION AND PROPERTIES OF CLAY-POLYMER COMPLEXES

B.K.G. THENG

*Soil Bureau, Department of Scientific and Industrial Research,  
Lower Hutt, New Zealand*



ELSEVIER SCIENTIFIC PUBLISHING COMPANY  
Amsterdam Oxford New York 1979

ELSEVIER SCIENTIFIC PUBLISHING COMPANY  
335 Jan van Galenstraat  
P.O. Box 211, 1000 AE Amsterdam, The Netherlands

*Distributors for the United States and Canada:*

ELSEVIER/NORTH-HOLLAND INC.  
52, Vanderbilt Avenue  
New York, N.Y. 10017

Library of Congress Cataloging in Publication Data

Theng, B. K. G.  
Formation and properties of clay-polymer complexes.

(Developments in soil science ; v. 9)

Bibliography: p.

Includes index.

1. Clay minerals. 2. Organic geochemistry.  
3. Soil chemistry. I. Title. II. Series.

QE389.625.T48

631.4\*17

78-13704

ISBN: 0-444-41706-0 (Vol. 9)

ISBN: 0-444-40882-7 (series)

© Elsevier Scientific Publishing Company, 1979.

All rights reserved. No part of this publication may be reproduced, stored in a retrieval system or transmitted in any form or by any means, electronic, mechanical/photocopying, recording or otherwise, without the prior written permission of the publisher, Elsevier Scientific Publishing Company, P.O. Box. 330, Amsterdam, The Netherlands.

Printed in The Netherlands

6

TABLE 1.1

Classification scheme for the crystalline clay minerals and related phyllosilicates (from Mackenzie and Mitchell, 1966)

Class	Type	Formula unit charge ( $x$ )	Group	Series
Phyllosilicates or layer silicates	1 : 1	~0	Kaolinite	Diocahedral
			Serpentine	Triocahedral
	2 : 1	~0	Pyrophyllite—talc	Diocahedral Triocahedral
		~0.25–0.6	Smectite or Montmorillonite	Diocahedral Triocahedral
		~0.6–0.9	Vermiculite	Diocahedral Triocahedral
		~0.9	Illite	Diocahedral Triocahedral
		~1.0	Mica	Diocahedral Triocahedral
		~2.0	Brittle mica	Diocahedral Triocahedral
	2 : 1 : 1	Variable	Chlorite	Diocahedral Di-tri-octahedral Triocahedral
Pseudo-layer silicates <sup>b</sup>	(2 : 1)	~0.1	Palygorskite—sepiolite <sup>c</sup>	Di-tri-octahedral Triocahedral

<sup>a</sup> Only the more common are listed. The nature of isomorphous substitution indicated refers to the predominant cation types involved.

<sup>b</sup> This is the name recommended by the Nomenclature Committee of Association International pour l'Étude des Argiles (AIPEA), Pedro (1970), replacing the term "chain-lattice silicates".

<sup>c</sup> The name "hormite" for this subdivision has been rejected by the AIPEA Nomenclature Committee.

<sup>d</sup> See text.

## d related phyllosilicates (from

p	Series	Species	Structural varieties <sup>a</sup>	Chemical varieties <sup>a</sup>
inite	Dioctahedral	Kaolinite	Kaolinite Nacrite Dickite b-Axis disordered kaolinite	
entine	Trioctahedral	Halloysite Antigorite Chrysotile		Metahalloysite (dehydrated) <sup>d</sup> Amesite (Fe <sup>2+</sup> ) Cronstedtite (Fe <sup>2+</sup> , Fe <sup>3+</sup> )
phyllite	Dioctahedral Trioctahedral	Pyrophyllite Talc		Minnesotaite (Fe <sup>2+</sup> , Fe <sup>3+</sup> , Al <sup>3+</sup> , H <sup>+</sup> )
ctite or tmorillonite	Dioctahedral Trioctahedral	Montmorillonite Saponite		Beidellite (Al <sup>3+</sup> for Si <sup>4+</sup> ) Nontronite (Fe <sup>3+</sup> for Al <sup>3+</sup> ) Volkonskoite (Cr <sup>3+</sup> for Al <sup>3+</sup> ) Sauconite (Zn <sup>2+</sup> for Mg <sup>2+</sup> ) Hectorite (Li <sup>+</sup> for Mg <sup>2+</sup> )
miculite	Dioctahedral Trioctahedral	Vermiculite Vermiculite		
e	Dioctahedral Trioctahedral	Illite Lepidolite		
a	Dioctahedral Trioctahedral	Muscovite Phlogopite	2M, 3H, 1M 1M, 2M, etc	Paragonite (Na <sup>+</sup> for K <sup>+</sup> ) Biotite (Fe <sup>3+</sup> for Al <sup>3+</sup> ) Lepidolite (Li <sup>+</sup> for Al <sup>3+</sup> ) Zinnwaldite (Li <sup>+</sup> , Fe <sup>2+</sup> )
tile mica	Dioctahedral Trioctahedral	Margarite Clintonite		
lorite	Dioctahedral Di-tri-octahedral Trioctahedral	Donbassite Sudoite Pennine Clinochlore		
lygorskite- iolite <sup>c</sup>	Di-tri-octahedral Trioctahedral	Falygorskite Sepiolite		Xylotile (Fe <sup>3+</sup> for Al <sup>3+</sup> )

omorphous substitution indicated

s Committee of Association Inter-  
1970), replacing the term "chain-

acted by the AIPEA Nomenclature



## Glycol Ethers Nomenclature

These tables explain the nomenclature and contain property and use information for DOW glycol ether products.

Table A: Nomenclature of E-Series Products

PRODUCT	CHEMICAL NAME	FORMULA	CA <sup>1</sup> INDEX NAME	CAS <sup>2</sup> NO. <sup>3</sup>
Methyl CARBITOL™ Solvent	Diethylene Glycol Monomethyl Ether	$\text{CH}_3(\text{OCH}_2\text{CH}_2)_2\text{OH}$	Ethanol, 2-(2-methoxy-ethoxy)-	111-77-3 <sup>(2)</sup>
Methoxytriglycol	Triethylene Glycol Monomethyl Ether	$\text{CH}_3(\text{OCH}_2\text{CH}_2)_3\text{OH}$	Ethanol, 2-[2-(2-methoxyethoxy)ethoxy]-	112-35-6
CARBITOL Solvent	Diethylene Glycol Monoethyl Ether	$\text{C}_2\text{H}_5(\text{OCH}_2\text{CH}_2)_2\text{OH}$	Ethanol, 2-(2-ethoxyethoxy)-	111-90-0
Ethoxytriglycol	Triethylene Glycol Monoethyl Ether	$\text{C}_2\text{H}_5(\text{OCH}_2\text{CH}_2)_3\text{OH}$	2-(2-(2-Ethoxyethoxy)ethoxy)ethanol	112-50-5
Propyl CELLOSOLVE™ Solvent	Ethylene Glycol Monopropyl Ether	$\text{C}_3\text{H}_7\text{OCH}_2\text{CH}_2\text{OH}$	2-(Propyloxy)ethanol	2807-30-9
Butyl CELLOSOLVE Solvent	Ethylene Glycol Monobutyl Ether	$\text{C}_4\text{H}_9\text{OCH}_2\text{CH}_2\text{OH}$	Ethanol, 2-butoxy-	111-76-2
Butyl CARBITOL Solvent	Diethylene Glycol Monobutyl Ether	$\text{C}_4\text{H}_9(\text{OCH}_2\text{CH}_2)_2\text{OH}$	Ethanol, 2-(2-butoxy-ethoxy)-	112-34-5
Butoxytriglycol	Triethylene Glycol Monobutyl Ether	$\text{C}_4\text{H}_9(\text{OCH}_2\text{CH}_2)_3\text{OH}$	Ethanol, 2-[2-(2-butoxy-ethoxy)ethoxy]-	143-22-6
Hexyl CELLOSOLVE Solvent	Ethylene Glycol Monohexyl Ether	$\text{C}_6\text{H}_{13}\text{OCH}_2\text{CH}_2\text{OH}$	2-Hexyloxyethanol	112-25-4
Hexyl CARBITOL Solvent	Diethylene Glycol Monohexyl Ether	$\text{C}_6\text{H}_{13}(\text{OCH}_2\text{CH}_2)_2\text{OH}$	2-(2-Hexyloxyethoxy)ethanol	112-59-4
ECOSOFT™ PB Solvent	Polyethylene Glycol Monobutyl Ether			9004-77-7
ECOSOFT PE Solvent	Polyethylene Glycol Monoethyl Ether			27879-02-8
ECOSOFT PH Solvent	Polyethylene Glycol Monohexyl Ether			31726-34-8
DOWANOL* EPh Glycol Ether	Ethylene Glycol Phenyl Ether	$\text{C}_6\text{H}_5\text{OC}_2\text{H}_4\text{OH}$	Ethanol, 2-phenoxy-	122-99-6
DALPAD* A Coalescing Agent	Ethylene Glycol Phenyl Ether	$\text{C}_6\text{H}_5\text{OC}_2\text{H}_4\text{OH}$	Ethanol, 2-phenoxy-	122-99-6
Butyl CELLOSOLVE Acetate Solvent	Ethylene Glycol n-butyl Ether Acetate	$\text{C}_4\text{H}_9\text{OCH}_2\text{CH}_2\text{OC}(\text{O})\text{CH}_3$	Ethanol, 2-butoxy-, acetate	112-07-2
Butyl CARBITOL Acetate Solvent	Diethylene Glycol n-butyl Ether Acetate	$\text{C}_4\text{H}_9\text{O}(\text{CH}_2\text{CH}_2\text{O})_2\text{C}(\text{O})\text{CH}_3$	Ethanol, 2-(2-butoxyethoxy)-, acetate	124-17-4

<sup>1</sup> Chemical Abstract Index (American Chemical Society).

<sup>2</sup> Chemical Abstract Service (American Chemical Society).

<sup>3</sup> CAS No. for major component. Refer to MSDS for detailed CAS No. Listing.

Table B: Nomenclature of P-Series Products

PRODUCT	CHEMICAL NAME	FORMULA	CA <sup>1</sup> INDEX NAME	CAS <sup>2</sup> NO. <sup>3</sup>
DOWANOL* PM Glycol Ether	Propylene Glycol Methyl Ether	$\text{CH}_3\text{OC}_3\text{H}_6\text{OH}$	2-Propanol, 1-methoxy-	107-98-2
DOWANOL DPM Glycol Ether	Dipropylene Glycol Methyl Ether	$\text{CH}_3\text{O}(\text{C}_3\text{H}_6\text{O})_2\text{H}$	Propanol, (2-methoxy-methylethoxy)-	34590-94-8
DOWANOL TPM Glycol Ether	Tripropylene Glycol Methyl Ether	$\text{CH}_3\text{O}(\text{C}_3\text{H}_6\text{O})_3\text{H}$	2-Propanol, 1-[2-(methoxy-1-methylethoxy)-1-methylethoxy]-	25498-49-1
DOWANOL PMA Glycol Ether	Propylene Glycol Methyl Ether Acetate	$\text{CH}_3\text{OC}_3\text{H}_6\text{OOCCH}_3$	2-Propanol, 1-methoxy,-Acetate	108-65-6
DOWANOL DPMA Glycol Ether	Dipropylene Glycol Methyl Ether Acetate	$\text{CH}_3\text{O}(\text{C}_3\text{H}_6\text{O})_2\text{OCCH}_3$	Propanol, (2-methoxy-methylethoxy), -Acetate	88917-22-0
DOWANOL PnP Glycol Ether	Propylene Glycol n-Propyl Ether	$\text{C}_3\text{H}_7\text{OCH}_2\text{CH}(\text{CH}_3)\text{OH}$	2-Propanol, 1-propoxy	1569-01-3
DOWANOL DPnP Glycol Ether	Dipropylene Glycol n-Propyl Ether	$\text{C}_3\text{H}_7\text{O}[\text{CH}_2(\text{CH})\text{CH}_3\text{O}]_2\text{H}$	2-Propanol, 1-(1-methyl-2-propoxyethoxy)-	29911-27-1
DOWANOL TPnP Glycol Ether	Tripropylene Glycol n-Propyl Ether	$\text{C}_3\text{H}_7\text{O}[\text{CH}_2(\text{CH})\text{CH}_3\text{O}]_3\text{H}$	Propanol, (1 or 2-methyl-2-(methyl(-2-propoxy ethoxy) ethoxyl)-	96077-04-2
DOWANOL PnB Glycol Ether	Propylene Glycol n-Butyl Ether	$\text{C}_4\text{H}_9\text{OCH}_2\text{CH}(\text{CH}_3)\text{OH}$	2-Propanol-1-butoxy	5131-66-8
DOWANOL DPnB Glycol Ether	Dipropylene Glycol n-Butyl Ether	$\text{C}_4\text{H}_9\text{O}[\text{CH}_2(\text{CH})\text{CH}_3\text{O}]_2\text{H}$	2-Propanol, 1-(2-butoxy-1-methylethoxy)-	29911-28-2
DOWANOL TPnB Glycol Ether	Tripropylene Glycol n-Butyl Ether	$\text{C}_4\text{H}_9\text{O}[\text{CH}_2(\text{CH})\text{CH}_3\text{O}]_3\text{H}$	Propanol, [2-(2-butoxy methylethoxy) methylethoxy]-	55934-93-5
DOWANOL PPh Glycol Ether	Propylene Glycol Phenyl Ether	$\text{C}_6\text{H}_5\text{OC}_3\text{H}_6\text{OH}$	2-Propanol, 1-phenoxy-	770-35-4
PROGLYDE* DMM Glycol Diether	Dipropylene Glycol Dimethyl Ether	$\text{CH}_3\text{O}(\text{C}_3\text{H}_6\text{O})_2\text{CH}_3$	Propane, oxybis [methoxy]-	111109-77-4

<sup>1</sup> Chemical Abstract Index (American Chemical Society).<sup>2</sup> Chemical Abstract Service (American Chemical Society).<sup>3</sup> CAS No. for major component. Refer to MSDS for detailed CAS No. Listing.

- [8] H. Liu, N. Toshima, *J. Chem. Soc., Chem. Commun.* 1992, 16, 1095.  
 [9] A. E. Woodward in *Atlas of Polymer Morphology*, Carl Hanser Verlag, Munich, 1989, Ch. 6.  
 [10] A. Roescher, M. Möller, unpublished results.  
 [11] C. v. Fragsstein, H. Römer, *Z. Phys.* 1958, 151, 54.  
 [12] I. A. Creighton, D. G. Eadon, *J. Chem. Soc. Faraday Trans.* 1991, 87, 3581.  
 [13] H. Künstle, *Block Copolymer Composites with Semiconductor Nanocrystals*, Ph.D. Thesis, University of Twente, Enschede 1993, p. 21.

## New Polymer Electrolyte Nanocomposites: Melt Intercalation of Poly(ethylene oxide) in Mica-Type Silicates\*\*

By Richard A. Vaia, S. Vasudevan, Włodzimierz Krawiec, Lawrence G. Scanlon, and Emmanuel P. Giannelis\*

Batteries based on polymer electrolytes are the subject of active R&D competition worldwide. One of the most promising ways to improve the electrochemical performance of polymer electrolytes is by the addition of inorganic fillers.<sup>[1-4]</sup> The resulting composite polymer electrolytes (CPE) display enhanced conductivity, mechanical stability and improved interfacial stability towards electrode materials. Despite the improved properties of CPE, however, their application in rechargeable lithium batteries is still hindered by low ionic conductivity at ambient temperature, low lithium transport number and difficulties in processing.

Polymer nanocomposites might be an alternative to conventional CPE. Because of the significantly reduced dimensions of the filler and the polymer matrix (1–100 nm), nanocomposites often exhibit new and improved properties, when compared to their micro- or macrocomposite counterparts. One of the most promising ways to synthesize polymer nanocomposites is by intercalating polymers in layered inorganic hosts.<sup>[5-21]</sup> Previous efforts have focused on a) intercalation of a suitable monomer followed by polymerization or b) polymer intercalation from solution.

We have recently reported a more versatile and environmentally benign approach based on direct polymer melt intercalation.<sup>[22]</sup> The process involves heating the polymer with an alkyl ammonium-exchanged layered silicate above the melting or glass transition temperature for crystalline or amorphous polymers, respectively. In this paper we report on direct polymer intercalation of poly(ethylene oxide), PEO, in Na<sup>+</sup> or Li<sup>+</sup>-exchanged layered silicates and describe the properties of the resulting nanocomposites.

[\*] Prof. E. P. Giannelis, Dr. R. A. Vaia, Dr. S. Vasudevan  
 Department of Materials Science and Engineering  
 Cornell University, Bard Hall  
 Ithaca, NY 14853 (USA)  
 Dr. W. Krawiec, Dr. L. G. Scanlon  
 Wright Laboratory  
 Wright-Patterson Air Force Base, OH 45433 (USA)

[\*\*] This work was sponsored in part by Corning, Inc., and by generous gifts from Xerox and Southern Clay Products. RAV is supported by a DoD Fellowship. We benefited from the use of MRL Central Facilities funded by the National Science Foundation.

Intercalation of PEO in layered silicates is accomplished by heating the polymer with the host at 80 °C. For example, 0.28 g of PEO ( $M_w = 100\,000$ , PolySciences), and 0.72 g of Na<sup>+</sup>-montmorillonite (SWy-1, University of Missouri Clay Source Repository, cation exchange capacity 80 meq/100 g) were thoroughly mixed in an agate mortar, formed into a pellet using a hydraulic press and a pressure of 70 MPa, and heated at 80 °C in ambient atmosphere.<sup>[23]</sup> Although we focus on Na<sup>+</sup>-montmorillonite, both Na<sup>+</sup>- and Li<sup>+</sup>-exchanged forms behave similarly.

Figure 1 shows the X-ray diffraction pattern of PEO/Na<sup>+</sup>-montmorillonite hybrid before heating and after two and six hours at 80 °C, respectively. The X-ray pattern before

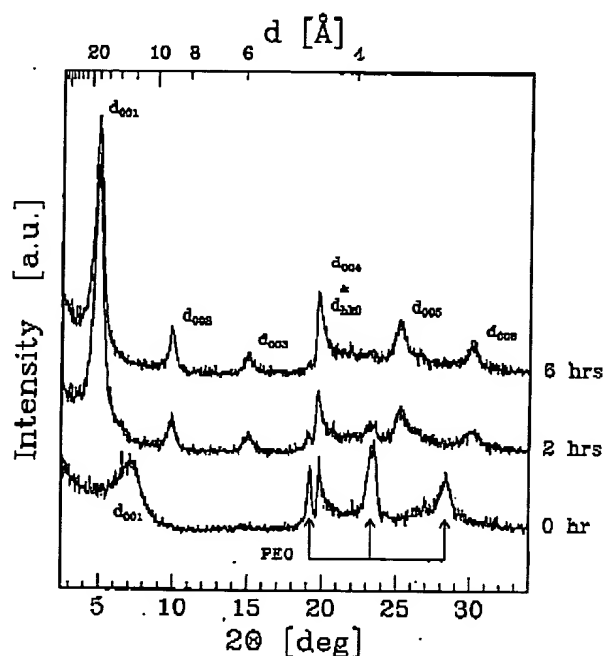


Fig. 1. X-ray diffraction pattern of PEO/Na-montmorillonite hybrid heated to 80 °C for 0, 2 and 6 hours.

any heating contains peaks characteristic of both pristine silicate ( $d = 11.4$  Å) and crystalline PEO (4.6, 3.8 and 3.2 Å). After heating to 80 °C, the intensity of the peaks corresponding to the unintercalated silicate and crystalline PEO is progressively reduced while a set of new peaks appears corresponding to the PEO-intercalated silicate. After six hours, only reflections corresponding to the PEO-intercalated silicate are observed signifying the completion of intercalation. The primary repeat unit ( $d$ -spacing) of 17.7 Å is identical to that previously obtained for PEO intercalation from solution.<sup>[9, 18–21]</sup>

Additional evidence for PEO intercalation is provided by Fourier transform infrared spectroscopy. The infrared spectrum of the intercalated sample contains absorptions characteristic of PEO superimposed on those from the layered silicate. In contrast to the spectrum of native PEO, however, the

band at  $\sim 2900\text{ cm}^{-1}$ , attributed to the polymer C-H stretching vibration, splits into a doublet at  $2910$  and  $2878\text{ cm}^{-1}$  in the intercalated spectrum. Similar behavior has been observed for the PEO-intercalated montmorillonite obtained by solution-assisted intercalation<sup>[9, 18-21]</sup> and is attributed to polymer-host interactions. The identical XRD pattern and infrared spectrum suggest that both melt and solution intercalation lead to the same intercalated phase.

Differential scanning calorimetry (DSC) studies offer further evidence for intercalation. Figure 2 compares the DSC traces of PEO/ $\text{Na}^+$ -montmorillonite after 0, 2 and 6 hours at  $80^\circ\text{C}$ . Both the 0 and 2 hour traces clearly show a distinct

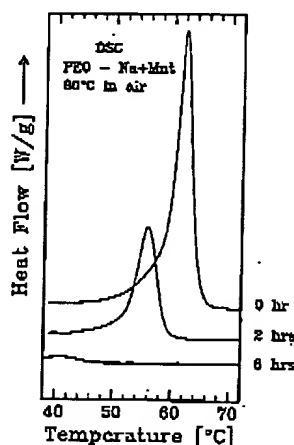


Fig. 2. DSC traces for PEO/ $\text{Na}^+$ -montmorillonite hybrids heated to  $80^\circ\text{C}$  for 0, 2 and 6 hours.

endotherm corresponding to the melting transition of crystalline PEO. As the intercalation reaction progresses, more PEO chains are intercalated and the area of the endotherm corresponding to the crystalline PEO is reduced. After six hours, the transition has largely vanished suggesting that all the PEO is intercalated—consistent with the X-ray diffraction data that shows only reflections corresponding to the PEO intercalated phase. The shallow hump in the six hour trace is most likely due to a small fraction of unintercalated crystalline polymer adsorbed on the external surfaces of the host particles. In addition to the decrease in the area of the endotherm, the transition also shifts to lower temperatures. As polymer intercalation advances, water molecules initially present in the silicate galleries are displaced to accommodate the incoming polymer chains. The displaced water molecules are likely incorporated in the PEO crystallites shifting the melting transition to lower temperatures.

A serious drawback in PEO electrolytes has been the precipitous decrease of conductivity (from  $10^{-4}$  to  $10^{-8}\text{ S/cm}$ ) below their melting temperature.<sup>[24]</sup> This decrease is due to the formation of crystallites that severely impede ionic mobility. Intercalation, therefore, offers a means to suppress polymer crystallization which, in turn, could enhance the conductivity of the electrolyte. Additionally, since in the nanocomposites the counter anions are the comparatively

immobile silicate layers, single ion conductor behavior is anticipated.

The ionic conductivity of PEO nanocomposites was determined from ac impedance measurements. Pellets were evacuated at  $100^\circ\text{C}$  before sandwiching between two metal lithium electrodes. To minimize moisture interference samples were prepared and loaded into sealed electrochemical cells in a dry box. AC ionic conductivity was calculated from the complex impedance plot using nonlinear computer fitting as described previously.<sup>[25]</sup> An Arrhenius plot of the in-plane ionic conductivity of the PEO/ $\text{Li}^+$ -montmorillonite nanocomposite containing 40 wt % polymer is shown in Figure 3. For comparison the conductivity of a conventional

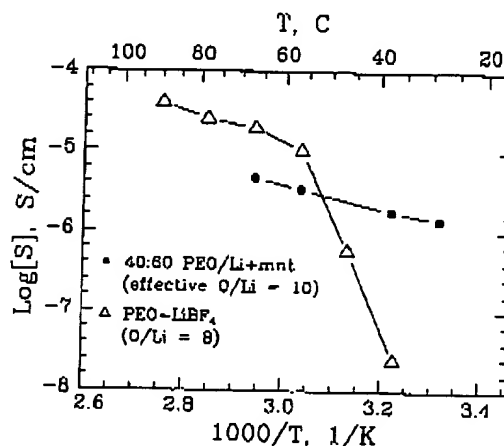


Fig. 3. Arrhenius plots of ionic conductivity for  $\text{LiBF}_4/\text{PEO}$  and  $\text{PEO}/\text{Li}^+$ -montmorillonite nanocomposite.

$\text{LiBF}_4/\text{PEO}$  electrolyte with a comparable O/Li ratio is also shown.<sup>[26]</sup> As expected, the conductivity of the  $\text{LiBF}_4/\text{PEO}$  electrolyte decreases several orders of magnitude below the melting temperature. In contrast, the conductivity of the nanocomposite exhibits only a weak temperature dependence over the same temperature range. In addition, the apparent activation energy in the nanocomposite ( $2.8\text{ kcal/mol}$ ) is similar to that of the molten polymer electrolyte suggesting that the mobility of  $\text{Li}^+$  in the nanocomposites is comparable to that in the bulk molten electrolyte. Furthermore, the out-of-plane conductivity of the hybrid is only an order of magnitude lower from the in-plane conductivity.

The conductivity of the melt-intercalated hybrid is much higher and more isotropic than that reported previously for PEO/silicate nanocomposites. Note, however, that those samples were prepared by solution intercalation and were thoroughly washed to remove excess polymer.<sup>[18-21]</sup> The enhanced ionic conductivity in our samples is probably due to the presence of excess polymer (40 vs. 30 wt %) that provides an easy conduction path between host particles. Removing excess polymer could lead to chain depletion from the edges of the silicate particles hindering the interparticle mobility of  $\text{Li}^+$  ions. Furthermore, the tendency of silicate



particles to orient parallel to the film surface when processed from solution is minimized in the dry-pressed samples used in this study leading to more isotropic properties.

In summary, polymer electrolyte nanocomposites have been synthesized by direct melt intercalation of PEO in layered silicates. Intercalation of the polymer chains in the silicate galleries greatly suppresses their tendency to crystallize. The conductivity of PEO/Li<sup>+</sup>-montmorillonite nanocomposite containing 40 wt. % PEO is  $1.6 \times 10^{-6}$  S/cm at 30 °C and exhibits a weak temperature dependence with an activation energy of 2.8 kcal/mol. The higher ionic conductivity at ambient temperature compared to conventional LiBF<sub>4</sub>/PEO electrolytes combined with their single ionic conductor character makes nanocomposites a promising electrolyte material.

Received: September 20, 1994  
Final version: October 31, 1994

- [1] S. Skaarup, K. West, B. Zachau-Crystiansen, B. *Solid State Ionics* 1980, 28-30, 375.
- [2] M. Nookola, L. G. Scanlon, R. A. Marsh, B. Kumar, A. K. Sircar, *J. Appl. Electrochem.*, in press.
- [3] W. Wiczkorek, *Mater. Sci. Eng.* 1992, B15, 108.
- [4] F. Capuano, F. Core, B. Scrosati, *J. Electrochem. Soc.* 1991, 138, 1918.
- [5] V. Mehrotra, E. P. Giannelis, *Solid State Commun.* 1990, 77, 155.
- [6] V. Mehrotra, E. P. Giannelis, in *Polymer Based Molecular Composites* (Eds: D. W. Shaefer, J. E. Mark) Mater. Res. Soc. Proc., Pittsburgh, PA 1990, 171.
- [7] E. P. Giannelis, V. Mehrotra, M. W. Russell, in *Better Ceramics Through Chemistry* (Eds: C. J. Brinker, D. E. Clark, D. R. Ulrich, B. J. Zolinski) Mater. Res. Soc. Proc. Pittsburgh, PA, 1990.
- [8] V. Mehrotra, E. P. Giannelis, *Solid State Ionics* 1992, 51, 115.
- [9] E. P. Giannelis, V. Mehrotra, O. Tse, R. A. Vaia, T.-C. Sung, in *Synthesis and Processing of Ceramics: Scientific Issues* (Eds: W. B. Rhine, T. M. Shaw, R. J. Gottshall, Y. Chen) Mater. Res. Soc. Proc. Pittsburgh, PA, 1992.
- [10] E. P. Giannelis, *J. Min. Met. Mater. Soc.* 1992, 44, 28.
- [11] M. G. Kanazidis, H. O. Marcy, W. J. McCarthy, C. R. Kannewurf, T. J. Marks, *Solid State Ionics* 1989, 32/33, 594.
- [12] M. G. Kanazidis, C. Wu, H. O. Marcy, C. R. Kannewurf, *J. Am. Chem. Soc.* 1989, 111, 4139.
- [13] G. Cao, T. E. Mallouk, *J. Solid State Chem.* 1991, 94, 59.
- [14] I. E. Pillion, M. E. Thompson, *Chem. Mater.* 1991, 3, 777.
- [15] W. M. R. Divigalpitiya, R. F. Frindt, S. R. Morrison, *J. Mater. Res.* 1991, 6, 1103.
- [16] L. F. Nazar, Z. Zhang, D. Zinkweg, *J. Am. Chem. Soc.* 1992, 114, 6239.
- [17] P. B. Messersmith, S. I. Stupp, *J. Mater. Res.* 1992, 7, 2599.
- [18] P. Aranda, E. Ruiz-Hitzky, *Adv. Mater.* 1990, 2, 545.
- [19] P. Aranda, E. Ruiz-Hitzky, *Chem. Mater.* 1992, 4, 1395.
- [20] P. Aranda, E. Ruiz-Hitzky, *Acta Polym.* 1994, 45, 59.
- [21] J. Wu, M. M. Lerner, *Chem. Mater.* 1993, 5, 835.
- [22] R. A. Vaia, H. Ishii, E. P. Giannelis, *Chem. Mater.* 1993, 5, 1694.
- [23] We have found that the extent of mixing significantly affects the reaction kinetics.
- [24] M. B. Armand, *Adv. Mater.* 1990, 2, 278.
- [25] W. Krawiec, L. G. Scanlon, J. P. Fellner, R. A. Vaia, S. Vasudevan, E. P. Giannelis, *J. Power Sources*, in press.
- [26] The O/Li ratio for the nanocomposite represents an effective ratio calculated from the cation exchange capacity of montmorillonite (80 meq/100 g) and the maximum amount of intercalated PEO (27 wt. %).

## Immobilization of Functionalized Lipids in a Random Poly(methacrylate) Copolymer Monolayer\*\*

By Klaus Lowack and Christiane A. Helm\*

Thin organic layers on solid substrates are often discussed as model membranes.<sup>[1]</sup> These model membranes are expected to be mechanically stable and they should exhibit well defined properties, which can be controlled over a wide range.

An important method for the production of thin organic films is the Langmuir-Blodgett transfer of monolayers at the air-water interface onto solid substrates. At the air-water interface, the monolayer can be controlled externally by varying the lateral density, the temperature, the ion content in the solution, the composition of the lipids and so on.<sup>[2]</sup> However, during transfer, the monolayer structure may undergo changes, an imperfect substrate induces defects within the monolayer, functionalized lipids may redistribute etc.

Usually, monolayers in the solid state are transferred via the Langmuir-Blodgett technique. For the purpose of model membranes lipid molecules in the solid state are rather inconvenient, since in general functionalized amphiphilic molecules do not mix evenly with frozen lipids arranged in ordered domains.<sup>[3]</sup> If the monolayer is in the fluid phase, the functionalized lipids are randomly and evenly distributed. However, now the guest molecules may diffuse within the model membrane leading to an uneven protein distribution under stress or if the external conditions are changed.<sup>[3-5]</sup> One way to obtain an even, random distribution of immobilized guest molecules is to stabilize the monolayer by polymerization. We present here such an amorphous monolayer. Functionalized amphiphilic molecules mixed into this monolayer are randomly distributed and immobile. Also, the monolayer is stable during Langmuir-Blodgett transfer from the air-water interface onto a solid substrate.

We have employed a poly(methacrylate) copolymer (PMA) with a hydrophilic and a hydrophobic substituent,  $x \approx y \approx 1$  (Fig. 1). The order of the two substituents is arbitrary. The copolymer is polydisperse. Figure 2 shows the relationship between the area per chain and the lateral pressure of the PMA monolayer at 20 °C. The lateral pressure starts to rise at  $\approx 72 \text{ Å}^2/\text{chain}$ , and increases steadily without any pronounced features. (The label of the x-axis is chosen in analogy to the isotherms of lipid molecules, where the alkyl chains are oriented more or less perpendicular to the

\* Dr. C. Helm, K. Lowack  
Institut für Physikalische Chemie, Johannes Gutenberg-Universität  
Jakob-Welder Weg 11, D-55099 Mainz (Germany)

\*\* We thank Prof. Helmuth Möhwald for his support. Anke Diederich, Heinrich Hans and Christel Müller were all helpful when experimental problems occurred. We thank Prof. Hyuk Yu for enlightening remarks. In the framework of the SFB 262, discussions with Dr. Jörg Baschnagel and Dr. Eckhard Bartsch were very stimulating. We thank Dr. Michael Völker, Bayer AG, for the generous gift of the copolymer. We appreciate the financial support of the Deutsche Forschungsgemeinschaft (DFG He 1616-5/1).